

CATALYSIS OF ALKENE AND ARENE HYDROGENATION BY THERMALLY ACTIVATED SILICA

Venkatasubramanian K. Rajagopal

Robert D. Guthrie

Department of Chemistry

University of Kentucky

Lexington, KY 40506

Burton H. Davis

Kentucky Center for Applied Energy Research

3572 Iron Works Pike, Lexington, KY 40511

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INTRODUCTION

In a recent study we described the hydrogenation of stilbene, α -methylstyrene and anthracene at 410 °C under 14 MPa of hydrogen or deuterium gas in the absence of added catalysts to give diphenylethane, cumene and 9,10-dihydroanthracene respectively.¹ As we were simultaneously working on the hydrolifuefaction of coal-model compounds attached to silica,² we became aware of work by Bittner, Bockrath and Solar³ which demonstrated catalytic effects of thermally activated silica in reactions involving H₂ and D₂. Using a pulse-flow microreactor, Bittner showed that after fumed silica is heated at 330 °C for 16 h in an argon stream it catalyzes the reaction H₂ + D₂ → 2 HD at temperatures as low as 120 °C. Moreover, this material catalyzes the hydrogenation of ethene to ethane at 150 °C and produces ethane-d₆ when D₂ is used as a flow gas. We became curious to see whether silica activated in this way would serve as a hydrogenation catalyst in a static reactor. Our results and additional information about the catalytic behavior of this material are described below.

EXPERIMENTAL

Hydrogenation Procedure. Approximately 300 mg of fumed silica (Cab-O-Sil M-5, Cabot Corporation) was placed in a length of (16 mm o. d.) glass tubing with a section of 1 - 2 mm capillary (ca. 16 cm long) attached to one end. Plugs of glass wool were placed between the silica powder and the tube exits. This assembly was heated in a tube furnace either at 330 °C or at 430 °C for 16 or more hours with argon flowing in the capillary tube and out through a ca. 2 mm hole in a stopper placed in the wide end. After this activation time, the tube was cooled to room temperature and a substrate was introduced maintaining the argon atmosphere during the addition process. The argon flow was then discontinued, the assembly evacuated, and the noncapillary end of the tube sealed under vacuum. Argon was readmitted and the reaction vessel was placed in a steel tube reactor under H₂ or D₂ pressure. The assembly was heated for the desired time period in a fluidized sand bath as described earlier.⁴ When the heating period was complete, the apparatus was cooled, the pressure released, the glass reactor section cracked open and the silica hydrolysed with ca. 30 mL of 1 M aqueous NaOH for ca. 15 h. At this point a measured aliquot of an external standard (biphenyl in CH₂Cl₂) was added. The aqueous solution was acidified and extracted three times with CH₂Cl₂. The glass reaction vessel was washed with CH₂Cl₂ and the washings combined with the extracts. The solvent was removed by rotary evaporation and the products analyzed by GC and GC/MS.

Exchange Experiments. Experiments to assess surface exchange were carried out in the same way as for the D₂ experiments described above except that instead of cracking the tube open after the D₂ treatment, a sample of phenol in benzene was added to the tube through the capillary opening using small diameter polyethylene tubing. Most of the benzene was pumped out and the capillary section sealed. The entire assembly was then placed in a tube furnace at 400 °C for 60 min. We have shown in other experiments that phenol-d₆ undergoes replacement of three of its ring deuterium atoms by hydrogen atoms on heating with Cab-O-Sil at temperatures above 140 °C.² After heating, the sealed tube was opened and the contents hydrolyzed in NaOH solution as described in the previous section. Control experiments showed that phenol could be recovered quantitatively from the hydrolysis workup and that the workup did not remove ring deuterium atoms.

RESULTS AND DISCUSSION

The results from hydrogenation of several alkenes in the presence of thermally-activated silica are given in Table I. The compound examined most extensively was stilbene (1,2-diphenylethene), **STB**.

Table I. Reaction of Unsaturated Compounds with D₂ or H₂ in the Presence and Absence of Thermally-Activated Silica.

Compound	T (°C)	Time (min)	D ₂ /H ₂	Silica ^a	% H-C-C-H	% C=C
<i>trans</i> - STB	300	30	D ₂	A	31	65
	300	50	D ₂	NA	7.2	90
	350	90	D ₂	A	91.2	7.3
	350	60	D ₂	none	1	98
	350	15	H ₂	none	<1	99 ^b
	350	100	H ₂	none	<1	99 ^c
Naphthalene	300	30	D ₂	A	1.2 ^d	98.5
	350	90	D ₂	A	1.5 ^d	98.5
1-Nonene	300	30	D ₂	A	36.3 ^e	35.3 ^e
Anthracene	350	80	D ₂	A	30	61
	350	60	D ₂	none	0.5	99.5
DPA ^f	350	40	D ₂	A	3.3 + 38.9 ^g	57.5 ^g
	300	90	D ₂	A	29 + 69 ^h	<1 ^h

^a A = Activated, NA = not activated. ^b *cis/trans* = 0.085. ^c *cis/trans* = 0.087. ^d Product appears to be mixture of dihydronaphthalene-*d*₂ and tetralin-*d*₄. ^e Remainder appears to be alkene isomers. ^f **DPA** = Diphenylacetylene. ^g Product contains 3.3% diphenylethane, **DPE**, and 38.8% mixed *cis*- and *trans*-**STB**, *cis/trans* = 0.26. This run was carried out with a different procedure, however, and it is not certain that all of the **DPA** was available for reaction. ^h Product is a mixture of **DPE** (29%) and **STB** with no significant amount of residual **DPA**. The **STB** shows *cis/trans* = 0.18.

It is clear that for **STB** there is no reaction with D₂ at 350 °C in the absence of silica and nearly complete hydrogenation to **DPE** after 90 min in the presence of activated silica. For the three runs carried out in the presence of silica, the deuterium distribution in the **DPE** produced was *d*₂ = 85.4%, *d*₃ = 6.0% *d*₄ = 3.5% in the first run, *d*₂ = 83.7%, *d*₃ = 10.6% *d*₄ = 2.0% in the second run, and *d*₂ = 63.3%, *d*₃ = 25.4% *d*₄ = 7.2% in the third run. The balance was a small amount of *d*₀ **DPE** present as an impurity in the **STB**. Thus, the product was mainly *d*₂ material which underwent additional deuteration at longer times and higher temperatures. ²H NMR showed that neither the **DPE** nor the **STB** remaining contained any significant amount of aromatic D whereas there was a prominent signal for the aliphatic D in the **DPE** produced. It will be noted that unactivated silica does catalyze the reaction to a lesser extent, but this might be expected in view of the fact that reaction temperatures are similar to activation temperatures. With naphthalene, there appears to be a small amount of dihydronaphthalene and tetralin being formed and these contain mainly 2 and 4 atoms of D respectively. However, we have not been able to increase the yield much above 1% by increases in time or temperature. Possible reasons for this situation are discussed below.

Nonene was picked as a prototypical nonaromatic alkene and it shows hydrogenation to nonane. The saturated material produced under these conditions is a mixture of ca. 64% nonane-*d*₀ and 36% nonane-*d*₃. The unreacted 1-nonene is mainly undeuterated, but the precision required to determine small amounts of D was unavailable due to extensive mass spectral fragmentation. Both of the nonene isomers, presumably *cis*- and *trans*-2-nonene are mainly *d*₁ material but contain about 30 % *d*₀ material. It thus seems likely that 1-nonene can isomerize under these circumstances and that at least part of the process does not involve the intermediacy of nonane-*d*₂.

The reaction is not limited to alkenes as anthracene can be reduced to dihydroanthracene, mainly with two atoms of D. Diphenylacetylene (**DPA**) is also

hydrogenated. At 350 °C, the STB produced is largely converted to DPE- d_4 . At 300 °C, substantial amounts of intermediate STBs are observed, mainly d_2 . The STB from these experiments seemed to be slightly enriched in the *cis*-isomer but the analysis was inherently imprecise due to the GC overlap between *cis*-STB and DPE. In order to provide more convincing evidence that the initial product of hydrogenation of DPA is *cis*-STB, the reaction temperature was lowered to 250 °C. Data for hydrogenation of DPA (with H₂) under these conditions is presented in Table II.

Table II. Yields of Products from Reaction of Diphenylacetylene with H₂ at 250 °C Over Thermally-Activated Cab-O-Sil.

	Time (min)				
	5	15	30	60 ^e	60 (<i>trans</i> -STB ^a)
DPA ^b	98.8	87.7	55.8	35.1	
<i>cis</i> -STB ^a	0.9	5.5	20.3	47.9	1.5
<i>trans</i> -STB	0.3	1.7	3.5	10.9	52.8
<i>cis/trans</i> ^c	3	3.3	5.8	4.4	
DPE ^d	<0.3	5.1	20.3	6.0	45.7

^a STB = Stilbene. ^b DPA = Diphenylacetylene. ^c Thermal equilibration gives a ratio of 0.1 at 350 °C. ^d DPE = Diphenylethane. ^e Reasons for the dramatic decrease in DPE formation in the 60 min run are uncertain. But, for this run the silica was activated at 430 °C rather than the 330 °C used for all of the other runs. This result is being checked.

It is clear from the data in Table II that the predominant product of hydrogenation of DPA at 250 °C is *cis*-STB by a ratio of at least 3 to 1. The equilibrium ratio of *cis*-/*trans*-STB has not been established at 250 °C, but the 5th and 6th runs of Table I show that at 350 °C the ratio is 0.086 and a lower value might be expected at 250 °C. Thus there seems little doubt that *cis*-STB is the kinetic product of DPA hydrogenation. This would seem to clearly rule out radical processes in which the two hydrogen atoms are transferred independently. The fact that we see none of the products expected from 1,2-diphenylethyl radicals: tetraphenylbutane or 1,1-diphenylethane also supports this conclusion. It appears that, whatever the active site for silica-catalyzed hydrogenation might be, it is similar to a metal-surface type catalyst in that H atoms are transferred in pairs and transferred in a stereoselectively *syn* fashion. It seems likely that the *trans*-STB produced in this reaction results from the thermal isomerization of the *cis*-isomer. Comparison of the STB runs in Table I carried out at 300 and 350 °C to the run in the last column of Table II shows that a temperature change of 100 °C does not have the effect on the conversion of STB to DPE that would be expected for a thermally activated reaction. For the thermal hydrogenation of STB studied earlier, reaction proceeds at a kinetically convenient rate at 410 °C but is not measurable after comparable times at 350 °C. It would thus seem a reasonable hypothesis that the rate-limiting step in the catalytic process has a low enthalpy of activation and may be controlled by geometric restrictions for access to the site.

It seemed logical that if D₂ is combining with silica in order to be activated for addition to unsaturated molecules, that the formation of OD bonds must be involved and, this being the case, that the process would provide a mechanism for exchange of the Si-OH groups on the silica surface with the D₂ atmosphere. In their microreactor process, Bittner did not observe formation of HD when D₂ was passed over the thermally-activated silica.³ Nevertheless, it seemed possible that this would happen under the higher pressures used in our experiments. To this end we carried out a series of experiments in which silica was activated then heated with D₂ followed by removal of the D₂ under vacuum and heating with phenol. Earlier work had shown that the *ortho* and *para*-positions of phenol undergo exchange with OH groups on the silica surface at temperatures above 140 °C.² After recovery from an aqueous workup the deuterium content of the phenol was determined by GC/MS analysis. Data are presented in Table III.

Although there is some scatter in the data, it is clear that heating with D₂ at temperatures above 200 °C introduces SiOD groups on the silica surface. Calculations based on the expected⁵ 4.5 SiOH groups per nm² of surface area suggest that roughly

75% of the surface SiOH groups are replaced by SiOD groups in the high temperature runs. The threshold temperature for the exchange reaction with D₂ appears to be between 200 and 250 °C. In the four runs carried out at 250 °C, the exchange with D₂ seemed about twice as great with silica which had undergone prior activation, however, the effect of activation on exchange was not as great as that on the STB reduction.

Table III. Deuterium Content of Phenol Exchanged^a with Cab-O-Sil (300 mg) Previously Treated with D₂ at 14 MPa at Various Temperatures.

Run	Activation?	Rxn. Time (min)	Rxn. Temp. °C	mg. PhOH	D/molecule
1	yes	20	350	40	0.30
2	yes	60	350	45	0.27
3	yes	120	350	42	0.38
4	yes	180	350	43	0.23
5	no	20	350	40	0.29
6	no	60	350	33	0.26
7	no	180	350	37	0.45
8	yes	60	250	16 (12)	0.31 (0.34)
9	no	60	250	19 (11)	0.18 (0.18)
10	yes	60	200	22	0.03
11	no	60	200	21	0.06

^a See Experimental section for details of the exchange experiments.

It remains uncertain at this point whether the mechanism for deuterium exchange of the silica surface hydroxyl groups and the mechanism for hydrogenation of alkenes are linked. At least for the alkene reaction, we can roughly estimate the concentration of active sites by the following experiment. Activated silica is heated with D₂, a process which Table III demonstrates will convert most of the surface SiOH groups to SiOD groups. The resultant deuterated silica (300 mg) which then has at least 0.33 mmole of D on the surface (after pumping off excess D₂) is heated with excess STB. The STB then contains a small amount of DPE-d₂. This amount is less than 0.015 mmole or roughly 10 % of the equivalents of D₂ present on the surface.

We find in some experiments that the thermally activated silica also is capable of catalyzing the hydrogenation of aromatic rings. The circumstances of this occurrence and the type of compound which is susceptible are under continuing investigation. As shown in Table I, a small amount of naphthalene is hydrogenated under the conditions described. To our astonishment, DPE is more extensively hydrogenated than naphthalene provided that the silica is thermally activated either for several days at 330 °C or at 430 °C for 16 h. We have found that the latter procedure gives reasonably reproducible results. Representative experiments are listed in Table IV. The reaction gives two products with gas chromatographic retention times which are very similar to DPE. With H₂ these products have mass spectra which match 1-cyclohexyl-2-phenylethane (CPE) and 1,2-dicyclohexylethane (DCE). Each is extensively deuterated and the ²H NMR spectrum of the mixture shows an envelope of purely aliphatic D atoms in the range of 1 to 1.5 ppm from TMS. The D content of the two reduction products suggests that much of the material arises from the replacement of the four benzylic H atoms in DPE as well as the addition of three D₂ molecules per reduced benzene ring. However, evidence for exchange at the aliphatic sites of the saturated rings is provided by the presence of up to CPE-d₁₈ and up to DCE-d₂₆. The DPE which is recovered is mainly DPE-d₄ but there is evidence for some exchange in the aromatic rings as well.

Astonishingly, when naphthalene is mixed with DPE and subjected to the conditions of Table IV, neither compound is hydrogenated and, moreover, the presence of naphthalene prevents even the exchange of the benzylic hydrogens as the DPE recovered contains very little deuterium. From a thermodynamic standpoint, it should be easier to hydrogenate one ring in naphthalene than the isolated phenyl rings of DPE. It

seems possible that naphthalene somehow blocks sites on the silica preventing its catalytic action, at least toward hydrogenation of DPE. Naphthalene does not block the hydrogenation of stilbene.

Table IV. Yields of Products from Reaction of Diphenylethane (DPE) with D₂ in the Presence of Thermally Activated Cab-O-Sil.

	Run 1	Run 2	Run 3
Activation Time	42 h	16 h	16 h
Activation Temp.	330 °C	430 °C	430 °C
Run Time	1 h	1 h	7 h
Run Temp.	350 °C	350 °C	350 °C
Yield CPE ^a	30.4%	22.6% ^e	37 % ^e
Yield DCE ^b	5%	5% ^f	13 % ^f
Recovery DPE ^c	64%	72% ^g	50 % ^g

^a CPE = 1-cyclohexyl-2-phenylethane. ^b DCE = 1,2-dicyclohexylethane. ^c DPE = 1,2-diphenylethane. ^e This was not completely resolved from DPE by GC, but its presence was clearly indicated by an envelope of ions in the mass spectrum ranging from d_6 to d_{18} with maximum intensity at d_{11} . The relative intensities of the ions in this envelope were similar for runs 2 and 3. ^f DCE was well resolved from DPE and CPE. Its mass spectrum showed an envelope of ions from d_{12} to d_{26} with maximum intensity at d_{19} . Again, relative intensities were similar for runs 2 and 3. ^g Recovered DPE showed an envelope of ions ranging from d_0 to d_{12} with maximum intensity at d_4 . In run 2, a substantial amount of d_0 material remained (slightly more than d_4). In run 3, the d_0 material had been largely consumed. However, the D distribution in the d_4 to d_{12} material was similar in the two runs.

SUMMARY

We have shown that even in bulk reactions, thermally-activated silica is a viable catalyst for the hydrogenation of alkenes and even of some arenes. Evidence for the stereoselectively *syn* nature of this process is found in the preferential formation of *cis*-hydrogenation of *cis*-STB from DPA. We have also shown that heating silica with D₂ at temperatures above 200 °C leads to exchange of surface OH groups in what may be a related process. Although mechanistic speculation may be premature, it seems reasonable that siloxane bonds formed when silica is heated are hydrogenated open by H₂ (or D₂) in a manner similar to that proposed for the reaction of ZnO with H₂.⁶ D₂ reacts with Si-(O)₂-Si to form DO-Si-O-Si-D which could possibly be the reactive species toward unsaturated carbon compounds. The strange effect of naphthalene suggests that the situation may be more complicated than this, however.

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